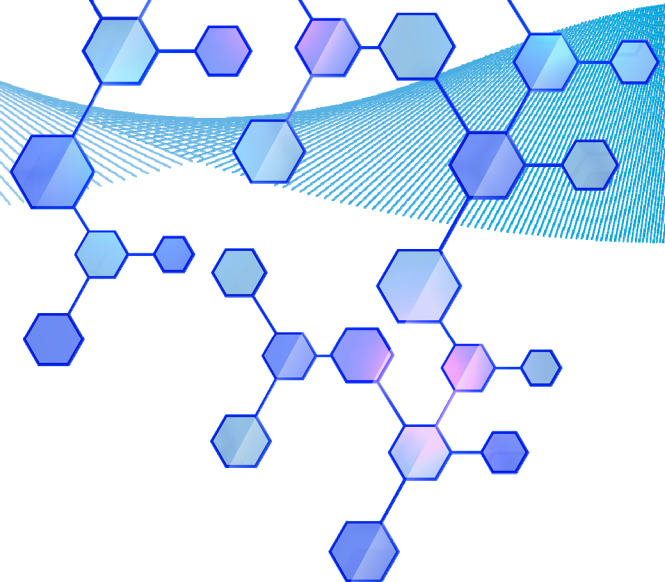




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OZONE AND ADVANCED OXIDATION SOLUTIONS FOR EMERGING POLLUTANTS OF CONCERN TO THE WATER AND THE ENVIRONMENT

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**Comparison of different advanced oxidation processes
used to the decomposition of organic pollutants in real thermal wastewater**

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Abstract

Thermal water often contains high amount of inorganic and/or organic contaminants, therefore its purification is required before the final disposal. Although phenolic and humic substances can be successfully eliminated from salty thermal wastewater by ozone treatment, the high radical scavenger ion content prevents the effective COD or TOC elimination from saline water. In the present study the purification of a real thermal wastewater (with high hardly oxidizable organic content and high carbonate concentration) was investigated comparing different AOPs, such as ozonation, Fenton reaction, and photo-Fenton reactions with different light sources. It was found, that ozone treatment was almost ineffective in COD and TOC elimination, but photo-Fenton reactions have given promising results. Investigating the effect of ferrous ion and hydrogen-peroxide concentration, the 1:25 molar ratio was found to be the most effective. Investigating the effects of different light sources, it was revealed that both the purification efficiency, and the COD or TOC elimination related “quantum yield” increased with the energy of photons due to their increased hydroxyl radical producing effect during the Fenton reactions.

Key-words: Ozonation, Fenton, photo-Fenton, thermal water, AOPs

Introduction

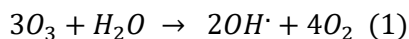
There are several thermal wells in the southern part of Hungary, where due to their high temperature, thermal waters are widely used as energy sources (domestic, agricultural or industrial utilization) [1]. As thermal waters often contain high amount of inorganic and/or organic compounds, their purification is necessary before the final disposal to natural waters or reuse.

High concentration of inorganic anions like Cl^- , SO_4^{2-} , HPO_4^{2-} , NO_3^- and HCO_3^- [2], and also cations like Na^+ , K^+ , Li^+ , NH_4^+ , Ca^{2+} [3], or organic compounds, especially the harmful phenols and phenol-derivatives may cause problems. Several studies have made an attempt to eliminate toxic organic compounds from waste thermal waters. It was found that application of granular activated carbon (GAC) is a promising way to remove aromatic pollutants like phenol, benzene, toluene, mesitylene below the detection limit ($<1 \mu\text{g/l}$) from thermal water, and the concentration of some inorganic substances, like NO_3^- -ions was successfully reduced by adsorption on mineral clays [4]. The general disadvantage of adsorption methods is that after separation of the organic contaminants do not diminish, further treatments are required.

Advanced oxidation processes (AOPs) can be effectively used to decompose any of the organic pollutants by generating highly-reactive radicals [5]. In contrast to conventional water purification methods, AOPs could offer a competent solution against hardly biodegradable, persistent and potentially toxic compounds. In addition, due to the high oxidation potential of the hydroxyl radicals ((between 2.8 V (at pH = 0) and 1.95 V (at pH =1 4)) enhanced biodegradability or complete mineralization of the organic pollutants can be achieved [5].

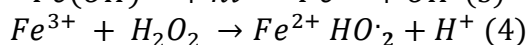
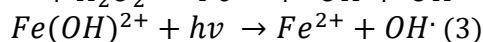
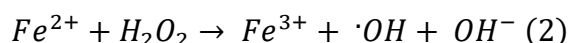
Ozone is one of the most commonly used oxidation reagent in water treatment. Depending on the experimental conditions, two different mechanisms must be considered. On the one hand

molecular ozone reacts at acidic pH (direct mechanisms) and takes part in electrophilic, nucleophilic and addition reactions. On the other hand at alkaline pH high amount of highly reactive hydroxyl radicals are generated according to Eq. (1).



Although, hydroxyl radicals are non-selective reagents for eliminating organic and inorganic compounds, dissolved inorganic ions and organic contaminants may act as radical scavengers and inhibit the radical reactions [6]. According to da Silva et al. [7], the inhibitory effect follows the sequence of $H_2PO_4^- > Cl^- > SO_4^{2-} > NO_3^- \sim CO_3^{2-}$.

Fenton and photo-Fenton reactions also could be a potent method to generate reactive radicals. During Fenton and photo-Fenton reactions inorganic salts of Fe^{2+} serve as catalyst and dissolved hydrogen-peroxide is used as oxidizing agent according to Eq. (2-4) [8,9]:



$Fe(OH)^{2+}$ is the most photoactive species generated at low pH (~2.9) and formation of Fe^{2+} from the complex produces extra hydroxyl radicals comparing to Fenton reaction. It has been also observed that aromatic compounds may catalyze the photo-Fenton reactions [10]. The main benefits of Fenton-like reactions compared with other AOPs systems are not only the availability of a cheap and non-toxic reagent, as iron, but also the easy care of H_2O_2 (which decomposition byproducts are also environment-friendly) and finally the easy application of the technology [11].

In an earlier work it was reported that the phenolic and humic substances were successfully eliminated from salty thermal wastewater by ozone treatment, however the reduction rate of chemical oxidation demand was very low [12], which can be related to the special matrix of thermal water: the high carbonate content which is a well-known radical scavenger. Although the ozonation could not significantly decrease the COD of high ionic content thermal water, some studies have been shown that Fenton and preeminently photo-Fenton treatments could be used to removal organic contamination in wide range of salinity water [13, 14]. In the present study purification of a real thermal wastewater (with high hardly oxidizable organic content and high carbonate concentration) was investigated comparing different AOPs, such as ozonation, Fenton reaction, and photo-Fenton reactions with different light sources.

Material and methods

Real thermal water was provided from South-Plain, Hungary (Szeged), by the company Floratom Ltd., Well K25). The initial temperature of the water is about 70 °C. The water was characterized by measuring the following parameters given in Table 1:

Characteristics of the thermal water	
Monitored parameters	Results
COD(Cr)	1470 ± 38 mg L ⁻¹
COD(Mn)*	41.3 mg L ⁻¹
TOC	494 ± 34 ppm
TC	1204 ± 89 ppm
Conductivity	5.01 mS cm ⁻¹
Phenol index*	4.365 ppm
Chloride*	368 mg L ⁻¹
pH	7.9
Hydrocarbonate ion*	2086 mg L ⁻¹
Ammonium ion*	18 mg L ⁻¹

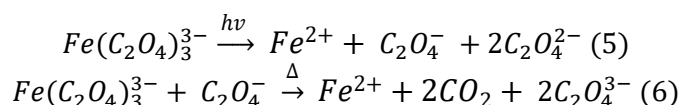
Table 1. Characteristics of the thermal water (*measured by an independent accredited laboratory)

For Fenton type treatments the pH value was set to be 3.5 (with H₂SO₄, 96 % w/w, Spektrum 3D, Hungary) in order to avoid the precipitation of Fe³⁺ as Fe(OH)₃ sludge. Reactions were carried out by using 250 cm³ thermal water with different molar ratios of Fe²⁺ (Fe(SO₄)-7H₂O) and H₂O₂ solution (30 % w/w, Spektrum 3D, Hungary) such as 1:12.5, 25, 50. Photo-Fenton treatments were carried out by using different immersed compact fluorescence light sources (UV tubes with intensity maximums at 360 or 254 or 254/180 nm and visible light emitting tube; 10 W; Lighttech, Hungary).

In case of ozonation experiments, O₃ was generated by a flow-type ozone generator (BMT 802N, Germany) and the absorbed volume was followed by measuring the absorbance of inlet and outlet at 254 nm (Biochrom WPA Biowave II, UK) using a 1.0 cm quartz flow-through cell. Experiments were carried out in a batch reactor filled with 500 mL thermal water solution and the generated ozone was bubbled through a diffuser, with 1 L min⁻¹ gas flow rate. Magnetic stirrer was continuously used at 350 rpm. 10 mL of samples were taken at 5, 10, 15, 20, 25 and 30 min during the ozonation. Residual dissolved ozone was purged by nitrogen gas (Messer 4.5) in order to obtain reliable chemical oxygen demand results.

Chemical oxygen demand was measured by the standard potassium dichromate oxidation method using standard test tubes (Hanna Instruments, USA) and applying digestions for 120 min at 150°C. In case of Fenton type treatments, before COD measurements the residual hydrogen peroxide was eliminated by addition of catalase enzyme (Sigma Aldrich). The amount of total organic carbon content was measured by a Torch TOC analyzer (Teledyne Tekmark, USA), equipped with an NDIR detector.

In order to obtain the exact light intensity of the UV light sources in the experimental reactor, iron-oxalate actinometry was performed. The method based on the formation of Fe²⁺ from ferric oxalate by the following Eq. (5-6) [15]:



In the presence of o-phenanthroline, iron(II) triphenanthroline is generated, and its concentration can be determined by measuring the light absorbance at 550 nm. 225 ml distilled water, 12.5 ml potassium oxalate (1.2 mol dm⁻³, VWR, Belgium, a.r.) and 12.5 ml iron(III) sulfate (0.2 mol dm⁻³, VWR, Belgium, a.r.) was filled in a batch reactor equipped with the light source. 1 ml sample was pipetted at every 20 seconds during two minute long period into a 10 ml flask, which already contained 6.5 ml distilled water, 2 ml o-phenanthroline (0.2 % w/w, Sigma Aldrich, >99%) and 0.5 ml sodium acetate (0.6 mol dm⁻³, VWR, Belgium, a.r.). Results of the different light intensity measured by actinometry are listed in Table 2.

Light source	Visible	UV (360 nm)	UV (254 nm)
Quantum yield ϕ	0.55	1.25	1.25
Light intensity (mol s ⁻¹)	1.56*10 ⁻⁶	1.41*10 ⁻⁶	6.49*10 ⁻⁷

Table 2. Light intensity of different light sources

To compare the performance of different AOPs, Oxygen-equivalent Chemical-oxidation Capacity (OCC, kg O₂ m⁻³) was used to quantify the oxidants used in the ozone treatment and Fenton processes, and was determined on the basis of stoichiometric calculations as [16]:

$$OCC = 1.000[O_3] = 0.471[H_2O_2] \quad (7)$$

where [O₃] is the demanded ozone concentration (kg O₃ m⁻³), [H₂O₂] is the demanded hydrogen peroxide concentration (kg H₂O₂ m⁻³).

Results and discussion

Oxidation ratios of different AOPs

In the first series of experiments COD and TOC elimination efficiency of ozone treatment in acidic and alkaline pH, Fenton, and photo-Fenton ($\lambda = 254$ nm) reactions (both carried out using 1:25 $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio) were compared. To obtain comparable data, the ratio of the eliminated pollutants (COD or TOC g m^{-3}) and the oxygen-equivalent chemical oxidation capacities (OCC, $\text{g O}_2 \text{ m}^{-3}$) were calculated and compared (Fig. 1.) It was found, that the applied amount of ozone (OCC=650 $\text{g O}_2 \text{ m}^{-3}$) did not decrease the COD and TOC, neither in pH = 3.5 nor in pH = 7.8, probably due to the high amount of the radical scavenger hydrogen carbonate. Fenton and photo-Fenton reactions were more effective; considerable COD and TOC decreases were observed after 4 h treatment (OCC= 942 $\text{g O}_2 \text{ m}^{-3}$). Comparing the COD and TOC results and calculating the TOC related theoretical oxygen demand (TOD, g m^{-3}) it can be seen, that in case of alkaline ozonation or photo-Fenton reaction, where hydroxyl radical generation is more expressed, the organic carbon was eliminated more effectively. This seems to be contradictory result, but taking into consideration the huge difference between the COD(Cr) and COD(Mn) values (Table 1), it can be explained by presence of hardly oxidizable organic pollutants; this means, that a significant part of pollutants cannot be oxidized by ozone (or potassium permanganate /potassium dichromate), only by hydroxyl radicals. Overall, photo-Fenton process resulted in the highest rate of organic matter reduction amongst the investigated AOPs methods.

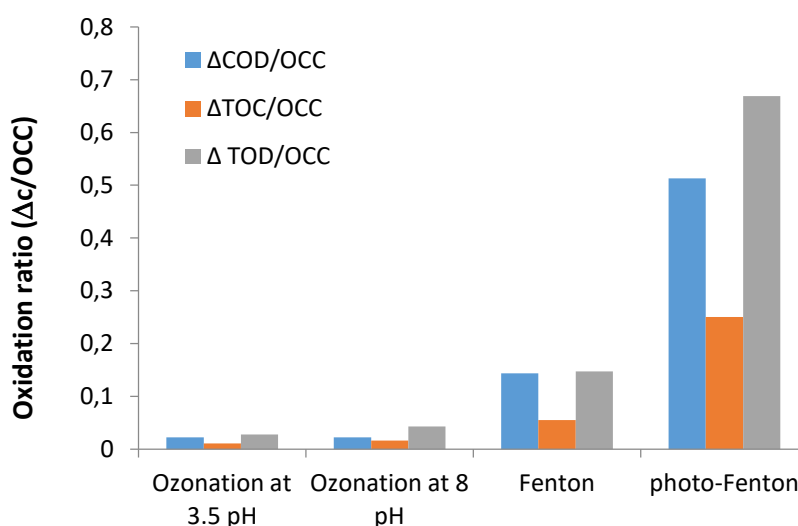


Figure 1. Oxidation ratio in case of different AOPs

Effect of Fe^{2+} dosage

As the photo-Fenton reaction was the most effective in elimination of organic pollutants from this water, the further experiments dealt to investigate the effect of Fe^{2+} and H_2O_2 -dosage during photo-Fenton reaction. At first, the effect of ferrous dosage on COD and TOC elimination efficiency was examined using three different initial Fe^{2+} concentrations. First, 1:25 molar ratio was chosen on the basis of results presented in the literature [17]. Ferrous ion concentration was 131 mg dm^{-3} , while the hydrogen-peroxide concentration was being kept 2000 mg dm^{-3} . After that, the amount of Fe^{2+} was doubled and then halved, which gave 2:25 (262 mg dm^{-3}) and 0.5:25 (65.5 mg dm^{-3}), respectively.

Figure 2.a shows the degradation of pollutants characterized by COD during photo-Fenton reactions (254 nm light source). The results indicate that the lowest Fe^{2+} concentration (0.5:25 molar ratio) was not enough to decrease the COD. The degradation rates were similar in the case of 1:25 and 2:25 molar ratio until 2 hours, but slightly decreased rate can be observed after 4 hours applying 2:25 molar ratio. The oxidation ratio (the amount of pollutant degraded by a unit of

oxidant) was the highest at 1:25 $[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2]$ ratio; the further increasing of ferrous ion concentration was not beneficial.

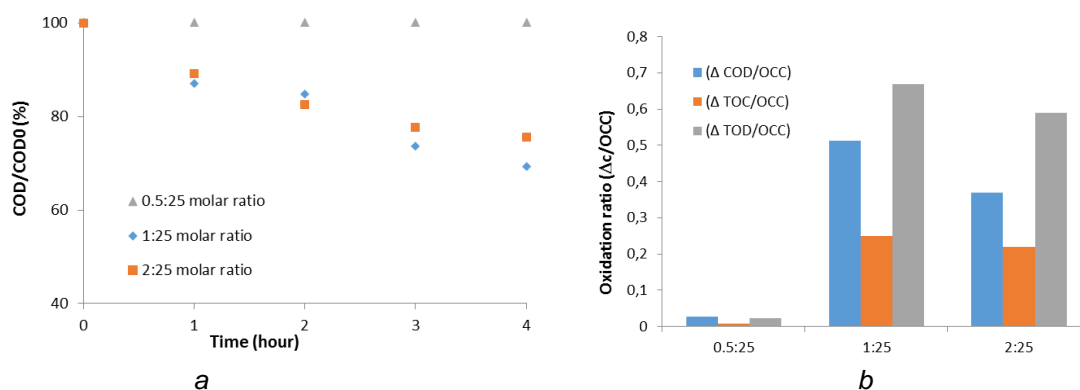


Figure 2. Effect of the ferrous ion concentration on the pollutant degradation by photo-Fenton (254 nm) treatments (a) and comparison of the oxidation rates (b) in presence of 2000 ppm hydrogen-peroxide, after 4 h treatment

Effect of H_2O_2 dosage

Hydrogen peroxide has a crucial role on Fenton reaction as the reactive hydroxyl radicals are generated from it by the Fe^{2+} . Figure 3 indicates the removal percentage of COD as a function of the reaction time during photo-Fenton process. Four different initial H_2O_2 concentrations were tested in our experiments, 400, 800, 2000, 4000 mg dm^{-3} which corresponds to 1:5, 1:10, 1:25, 1:50 $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratios respectively, where the ferrous ion concentration was constant 131 mg dm^{-3} .

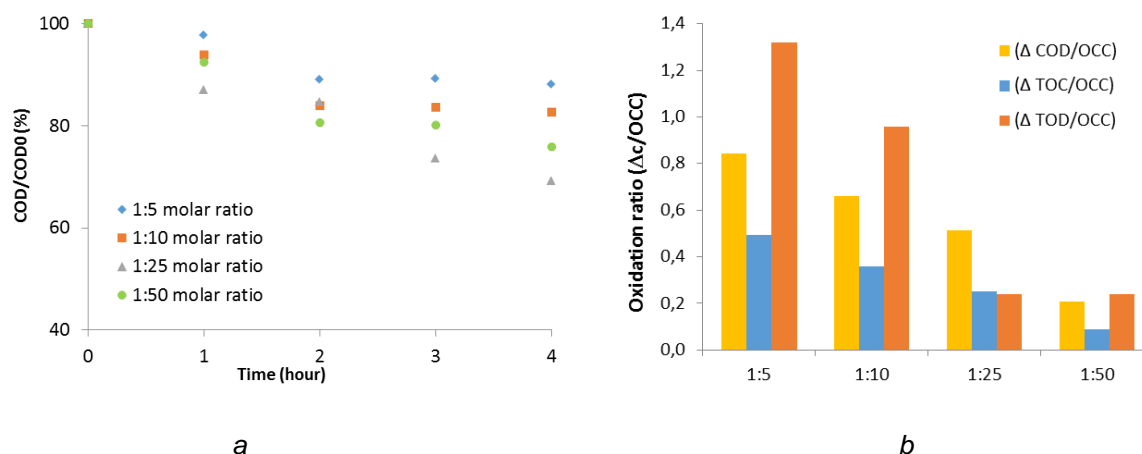


Figure 3. Effect of the H_2O_2 dosage (a) on the pollutant degradation by photo Fenton (254 nm) treatments and (b) relation of the COD/COD₀ and the TOC/TOC₀ removal rate

It was found that the COD elimination rate was increasing with H_2O_2 concentration to 2000 mg dm^{-3} values, but the further increase in hydrogen-peroxide concentration decreased the COD elimination rate. Very different results can be obtained by calculation the oxidation ratios (eliminated pollutant per unit of oxidant): by increasing the hydrogen-peroxide concentration, the amount of pollutants oxidized by a unit of oxidant is decreasing; the higher amount of oxidants cannot increase the degradation efficiency during the reactions. The most effective molar ratio was found to be 1:25 $[\text{Fe}^{2+}]:[\text{H}_2\text{O}_2]$.

The effect of the light sources

In the next series of experiments, the effect of the light source was investigated to reveal if the energy of visible light could be enough for an effective reaction. Photo-Fenton reactions with 1:25 $[Fe^{2+}]:[H_2O_2]$ molar ratio were carried out using different light sources, and compared to thermal Fenton reaction. The wavelength of the emitted light has significant effect on elimination efficiency; all of photo-Fenton reactions were more effective, than Fenton reaction, and UV light sources were more effective than visible light. In order to obtain quantitatively comparable results, the intensity of the light sources were measured, and “quantum yields” for COD and TOC elimination (mol COD or TOC eliminated by mol photon) were calculated (Fig.4.)

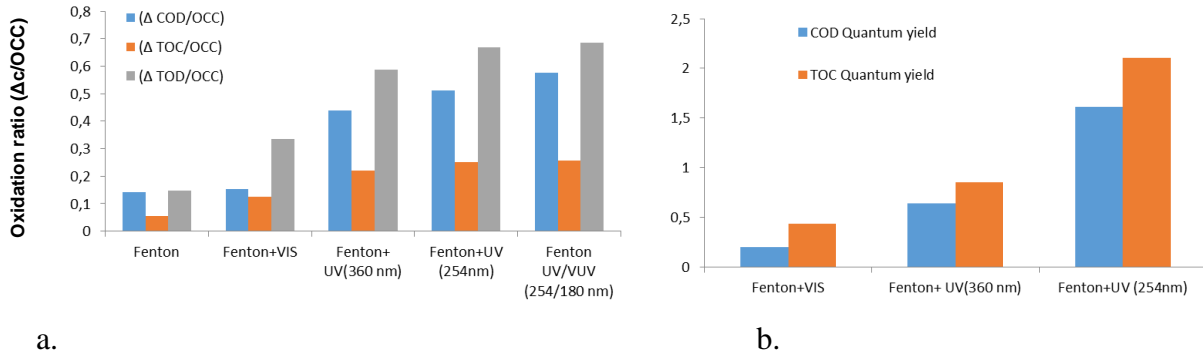
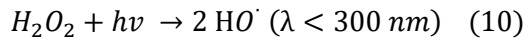
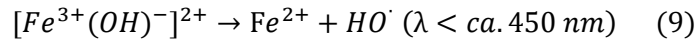
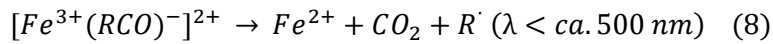
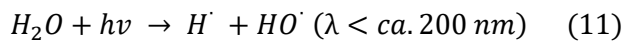


Figure 4. The degradation of pollutants after 4 h Fenton/photo-Fenton treatment: (a) oxidation ratios and (b) TOC and COD “quantum yields” in case of different treatments

The positive effect of irradiation may be caused by the photolysis of hydrogen peroxide or photoreduction of ferric ions, producing hydroxyl radicals. These reactions depend on the wavelength of the light [18]:



In case of the lamp emitting at 254/180 nm the VUV photolysis of water also can be taking into consideration:



In the visible range, comparing to thermal Fenton reaction, the Eqs 8-9 may take part, while in the UV range reactions of Eq 9 or also Eq 10 may contribute to hydroxyl radical generation, which is in accordance with the experienced increased “quantum yield” of the photons with higher energy. In case of UV/VUV light source only slight increasing in the efficiency was observed, probably due to the very short absorption pathway and high recombination rate of H^{\cdot} and OH^{\cdot} radicals. This result shows that photons with higher energy can be utilized with a dramatically higher yield by means of their hydroxyl radical generating reactions.

Conclusions

In this work purification of real waste thermal water was investigated by different advanced oxidation processes. The thermal water had very high ion content (mainly HCO_3^- and Cl^-), and relatively high organic content (phenols, hydrocarbons and humic substances). This composition of waste water resulted in a very complicated reaction system for advanced oxidation processes; where inorganic anions may inhibit the oxidation reaction of ozone and also the Fenton-like reactions, while aromatic compounds may catalyze them.

In this system the photo-Fenton reaction was found to be the most effective method for degradation of organic pollutants due to its high hydroxyl radical generation ability.

The investigation of the effect of different light sources (UV tubes with λ_{\max} = 360 or 254 or 254/180 nm and visible light emitting tube) also revealed, that both the purification efficiency, and the COD or TOC elimination “quantum yield” of photons increases with the energy of photons due to their hydroxyl radical producing reactions.

Acknowledgements

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